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Nuclear magnetic resonance studies on pentaerythritol-moleculer structure molecular reorientation and impurity diffusion

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The nuclear magnetic resonance spectra have been measured for the protons in pentaerythritol $(CH_2OH)_4C$ in the solid state between 94°K and 475°K (which is approaching the melting point 533°K). Spin lattice relaxation times have also been measured.

It has been found that the second moment (mean square-width) of the measured spectrum for the temperature at which the lattice is efectively rigid, viz., below 94°K, is consistent with a molecular structure having symmetry properties of the space group 14, tetrahedral bond angles, C–C bond length of 1.50Å, C–O bond length of 1.46Å and C–H bond length of 1.09Å with two molecules in a unit cell in a body centred tetrahedral crystal structure. The dimensions being $a = b = 6.07$Å and $c = 8.74$Å, in which the hydroxy hydrogen is closer to O_1 at (x, y, z) than to O_2 at $(y, \bar{x}, \bar{z})$. A line narrowing at about 235°K has been explained as an intra-molecular motion of OH group. The first transition at about 434°K is explained in terms of a general molecular reorientation about the symmetry axis. The second transition at about 453°K has been characterised as due to an impurity diffusion. The activation energy has also been computed to be 26°Kcal/Mole. Besides, molecular self-diffusion is also effective as a line narrowing agent. In addition inherent water impurity in the sample has been observed.

The calculations have shown that the fractional coordinates of the position of hydroxy hydrogen assigned by Hvoslef (1958) in his neutron dif fraction study are not consistent with his diagram.

1. INTRODUCTION

In certain cases the analysis of the variation of the nuclear magnetic resonance absorption line shape with temperature can give valuable information regarding both molecular structure and molecular motions in the solid state. This paper reports NMR. studies of solid pentaerythritol which were undertaken to gain information about the intramolecular and molecular motion in the solid state as well as to provide an N.M.R. check of molecular structure previously determined by X-ray, infra-red, Raman and neutron diffraction studies.

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2. Molecular Structure and H-Bonding

Pentaerythritol has the formula $C(CH_2OH)_4$ (figure 1a) and the molecular structure shown in figure 1b. It is an aliphatic alcohol which forms a tetragonal crystal and possesses the symmetry properties of the space group $(\overline{14})$. Early experiments by Mark & Weissenberg (1923) and Huggins & Bendricks (1926) appeard to be inconsistent with the tetrahedral distribution of the bonds. It was thought that the pentaerythritol possessed a pyramidal structure. Later work of Llewellyn *et al* (1937), Nitta & Watanbe (1937) and Cox, Cruickshank

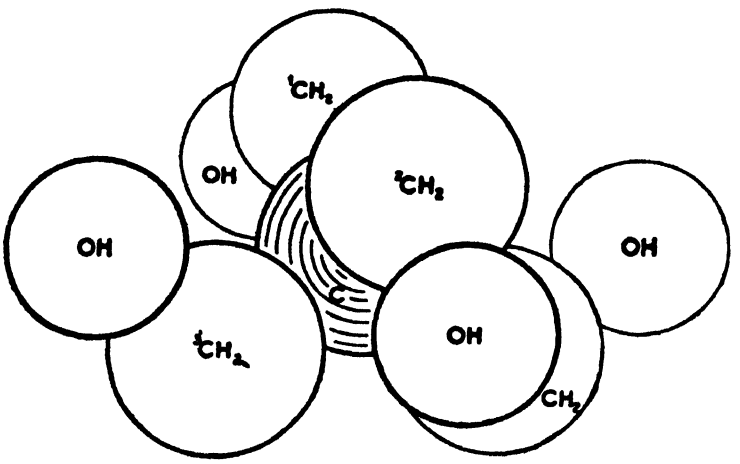

Fig. 1a. Model of pentaerythritol molecule.

Fig, 1b. Molecular structure of pentaerythritol. The atoms are labelled as follows : Black = Carbon, Grey = Oxygen, White = Hydrogen.

& Shiono (1958) however, discredited this conclusion and revealed that the molecule has a symmetrical form. They assumed a tetragonal distribution of the bonds around the central carbon atom. The cell is body centred having dimensions $a_0 = 6.10\text{Å} = b_0$ and $c = 8.73\text{Å}$ containing two molecules each of which possesses a fourfold alternating axis of symmetry parallel to C-axis. The central carbon atoms of these molecules lie at the corners and centre of the cell, through which axes of four fold rotatory inversion pass. The carbon atom of CH_2 group and oxygen atom of OH group lie in the general position and there are eight of each in the unit cell, four associated with each molecule and derivable from one another by the action of the axis of rotatory inversion. The central atom of one molecule is located at $(0, 0, 0)$. While the other is present at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Four CH_2 groups at the corners of an almost exact tetrahedron surrounding the central carbon atom with one pair of hydroxyl oxygen atoms puckered upwards and the other downwards. Each hydroxyl group is attached to its CH_2 by a bond making approximately the tetrahedral angle with the $C\text{-}CH_2$ link and is so directed that the four hydroxyl groups lie at the corners of a square of sides 2.69Å. The positions of the hydrogen atoms are more difficult to obtain from X-rays than those of the heavier atoms. The hydrogen position, therefore, remained undetermined. Jan Hvoslef (1958) using neutron diffraction method postulated four possibilities for the position of hydroxy hydrogen; either H atom is closer to the oxygen O_1 at (x, y, z) than to O_2 at (yxz) or H atom is closer to O_2 than O_1 or two half hydrogen atoms are placed between O_1 and O_2 constituting a disordered structure similar to that reported for heavy ice by Peterson & Levy (1957) or H atom has the same distance from both oxygen atoms. The results of parameters assuming tetrahedral angle were in good agreement with the X-ray results of previous investigators.

Jan Hvoslef supports model No. 1 and points out the anisotropy of the thermal vibration for the hydroxy hydrogens. No such anisotropy is found for other atoms. Nayar (1938) in his Raman studies and Ellis & Bath (1939) using infrared method have found evidence in support of assumed X-ray model. Besides later workers observed the usual broad absorption region around 1.5μ characteristic of a highly perturbed hydroxyl group, which according to Hvoslef does not satisfy the assumed square arrangement of OH groups in pentaerythritol, therefore some strain has to be assumed.

3. Experimental Details

3.1. *Sample*

The sample of pentaerythritol used in our investigations was obtained from British Drug House, London. High purity is essential for this work, as the effects of impurities can be very misleading (Rushworth 1952). The sample was transferred in a suitable glass tube to fit the nuclear resonance coil.

3.2. *Signal Detection and Measurement*

The proton resonance was observed in the field of approximitely 6000 gauss, which was supplied by a permanent magnet specially designed by Andrew & Eades at 25 Mc/sec. A conventional wide line spectrometer employing a standard signal generator, twin T bridge, cascade preamplifier and receiver was used to detect the resonance. The derivatives of broad absorption spectra were recorded using a record milliameter. The line-widths and second moments were determined from the absorption curve derivatives, the second moment values being corrected for the finite modulating field (Andrew 1953). The details of the apparatus used are described elsewhere (Gupta 1963). The spin-lattice relaxation time (T_1) measurements were made by Linder (1957) signal decay technique.

3.3. *Temperature Control*

Cryogenic equipment used was designed to investigate samples in the temperature range 4°K to 78°K. The cryostat which was provided with the pumping facilities was so designed that liquid air, liquid nitrogen and liquid helium could be used separately as the coolant depending upon the working temperature of the experiment. The temperature range 57°K and 78°K were covered by using liquid nitrogen boiling under reduced pressure. In studying the solid state phase transition it is essential to minimise temperature gradients over the sample and cryostat was designed with this in mind.

High temperature system consisted of electrical heating using voltage from a 60 volt battery. Electrical insulation was achieved by using a furnace cement (alumina). The heater was screwed at the bottom of the sample can, with this device the specimen and the specimen holder were in good thermal contact with the heater. The specimen holder was made of Fluon which has got a good electrical insulation and can stand high temperatures without burning or softening. A copper-constantan thermocouple was used to measure the temperature of the sample.

4. Experimental Results

4.1. *Second moment and line width*

Figure 2 shows the typical, derivative, traces below and above the transition temperature. From data such as these the plot of second moment versus temperature shown in figure 3 was derived. At low temperature from 94°K to nearly 235°K the second moment is constant at 28.1 gauss^2, presumably rigid lattice value. At temperature round about 268°K a dip is observed in the value of second moment and line width (figure 4).

As the temperature was increased above room temperature narrowing of the line started and at 434°K the observed second moment and line width reduced

to 11.8 gauss^2 and 5.0 gauss from its rigid lattice value 28.1 gauss^2 and 15.6 gauss respectively.

When sample was heated above 434°K the line started narrowing very rapidly. At about 453°K the second transition was observed and second moment value reduced to about 0.5 gauss^2.

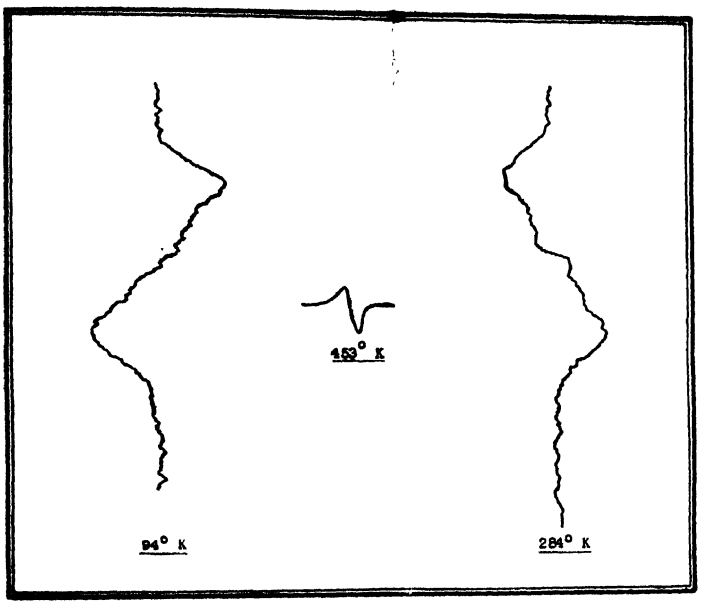

Fig. 2. Derivative traces for pentaerythritol. Scan rate is the same for each.

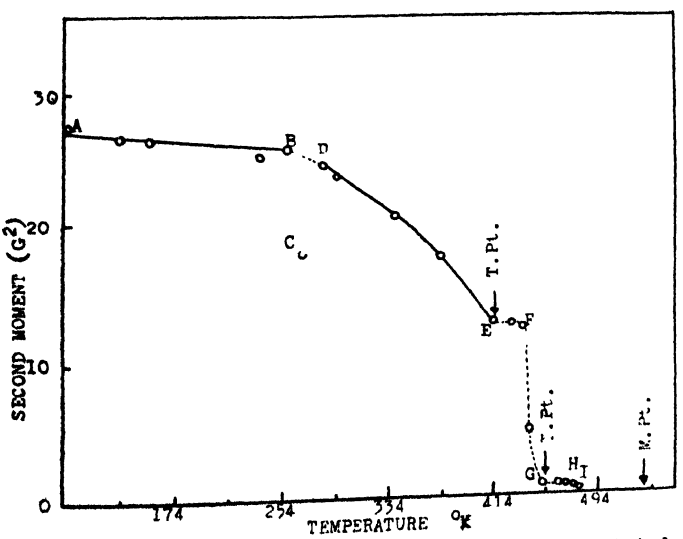

Fig. 3. Second moment versus temperature for pentaerythritol.

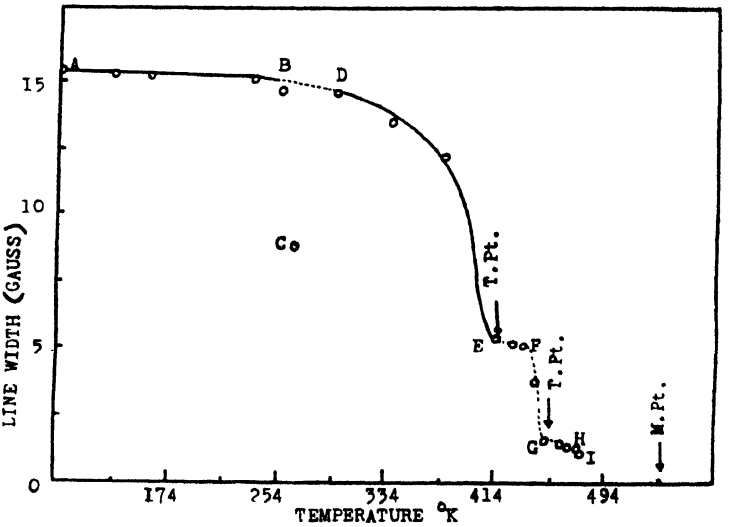

Fig. 4. Line Width versus temperature for pentaerythritol.

4.2. *Spin-lattice Relaxation Time*

The temperature variation of spin-lattice relaxation time T_1 has also been measured. The value of T_1 at liquid air temperature was about 54 seconds (figure 5) and that at room temperature about 4 seconds (figure 6). The rapid decrease in T_1 at high temperature is associated with the narrowing of the spectrum line.

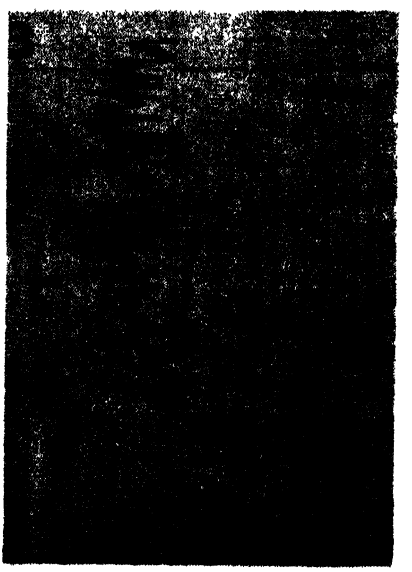

Fig. 5. Spin Lattice relaxation time at 94°K.

Fig. 6. Spin Lattice relaxation time at 284°K.

5. Calculations

5.1. *Rigid Lattice*

5.11. *Second Moment*

The rigid lattice second moment (S_0) was calculated from the theory of Van-Vleck (1948) for polycrystalline samples. The contribution (S_0) consists of two parts—intramolecular (S_1) and intermolecular (S_2) contributions. Intramolecular contributions to the second moment arise from the nuclei which reside in the same molecule and are calculated from the formula for the protons :

$$S_1 = \frac{6}{5}\frac{(I+1)^2}{I} N^{-1}\mu^2 \sum_{j>k} r_{jk}^{-6} \text{ gauss}^2$$

where I is the spin number, μ is the magnetic moment. N is the number of magnetic nuclei over which the sum is taken and r_{jk} is the distance between nucleus j and k. In our particular case using Bearden & Watts (1951), values the above equation simplfies to

$$S_1 = \frac{715.9}{N} \sum_{j>k} r_{jk}^{-1} \text{ gauss}^2$$

Theoretically determined intramolecular contribution alone, based on the assumed model of Jan Hvoslef (1958), in which he considered H atom belonging to hydroxy hydrogen group to be closer to O_1 than to O_2 is found to be abnormally high. The experimental rigid lattice second moment value is of the order of 28 gauss^2 which differs widely with the theoretically determined values. This obviously points out that assumed model may not be a correct one. The theoretical value of (S_1) suggested that hydroxy hydrogen should be well away from other protons inside the molecule and as such another possibility was considered in which hydroxy-hydrogen lies mid-way between the two oxygen atoms.

The new positions of the hydroxy-hydrogens were determined and with these values the intramolecular contribution to the second moment was calculated as about 11.7 gauss^2, a value which appeared to be reasonable.

The third possibility mentioned by Hvoslef (1956) two half hydrogens are placed between O_1 and O_2 constituting a disordered structure, has also been considered; with this assumed model the value of intramolecular contribution is obtained as 10.4 gauss^2.

An abnormally high value of second moment led us to check the proton coordinates determined by Hvoslef (1958). It was found that the fractional coordinates of hydroxy-hydrogens given by Hvoslef are not consistent with his diagram. The Z coordinates were correct, while X and Y coordinates were corrected as given in table 1 and intramolecular contribution is found to be 14.6 gauss^2 which appeared to be more reasonable.

Table 1

		X	Y	Z
Hydroxy-hydrogen	H	1.64497	2.37944	0.02622
	H	2.37944	−1.64497	−0.02622
	H	−1.64497	−2.37944	0.02622
	H	−2.37944	1.64497	−0.03633

After calculating the intramolecular contribution to the second moment for various possibilities of the position of the hydroxy hydrogen tedious calculations were avoided by making carefully scaled models using revised coordinates for hydroxy-hydrogen of the type of molecule shown in figure 2 with a view to determine inter-molecular radii for computations of the inter-molecular contribution to the rigid lattice second moment.

The intermolecular contribution due to interaction between any nucleus j in certain molecule with any other nucleus k in another molecule, could be broken into a Van-Vleck sum truncated at radius R, plus a terminal contribution for $r_{jk} >> R$ (Andrew 1955, Ibers &Stevenson 1958, Waugh 1958).

The terminal contribution was obtained by assuming the distribution of protons to be continuous at large value of r_{jk} and replacing the sum by an intergal, we have

$$S_2^{trunc.} = \frac{715}{N} \sum_i N_i \sum_j n_j^i \sum_k r_{jk}^{-6} \text{ gauss}^2.$$

The terminal contribution was found to be

$$S_2^{term} = \frac{715}{N} 4\pi N_p (3R^3 V)^{-1} \text{ gauss}^2,$$

where N_1 is the number of molecules on the i-th neighbour site, n is the number of j-th protons on the origin molecule which are equivalent with respect to an i-th neighbour, R is cut off radius and N_p is the number of protons per unit cell and V is the volume of the unit cell in Å^3.

Amongst various possibilities considered a reasonable value of the truncated contribution is found to be 12.29 ± 1 gauss^2 postulating hydroxy hydrogen is nearer to O_1 than O_2. The terminal contribution yielded a value of 0.15 gauss^2. Thus the theoretical rigid lattice value of second moment is found to be

$$(S_0) = 14.58 \pm 12.29 + 0.15 \pm 1 \text{ gauss}^2$$
$$= 27.02 \pm 1 \text{ gauss}^2.$$

The theoretical value of the second moment is in good agreement with the experimentally observed value of about 28.1 gauss^2.

5.2. *General Molecular Reorientation*

An examination of the lattice structure suggests that the molecular motion which may likely cause the narrowing of the absorption line, is the rotation of every molecule around the symmetry axis. Andrew & Eades (1953) pointed out that a rough value of the second moment for general reorientation of the molecule about the centre of gravity is given by the replacement of intramolecular distance r_{jk} in the Van-Vleck expression by centre to centre molecular separation i.e., concentrating all nuclear magnets at their molecular centre. It has been reported by workers that for molecules reorienting rapidly enough in random manner about their centres. this technique is exact. The intra-molecular contribution to the second moment becomes zero in the case of general reorientation. The second moment for general reorientation of molecule is thus given by

$$S_R = 715.9 N_0 \sum_j N_j R_j^{-6} \text{ gauss}^2,$$

where N_j is the number of j-th nearest neighbour and R_j is the centre to centre radius joining the original molecule and j-th nearest neighbour.

It is possible to compute S_R when the crystal structure changes from tetragonal to cubic at about 453°K by making use of the expression for the *bcc* lattice sum given by Torrey (1954).

$$\Sigma N_j R_j^{-6} = 24.045 C^{-6},$$

where C is the lattice parameter :

Thus, $$S \simeq \frac{715.9 . N_0 . 24.045}{C^6} \simeq 0.56 \text{ gauss}^2.$$

The theoretically estimated value of rotational second moment (0.56 gauss^2) is in good agreement with the experimentally observed value (0.5 gauss^2). It is therefore evident that the discontinuity obtained is due to the general molecular reorientation at about 453°K.

5.3. *Activation Energy and Rotational Frequency*

Gutowsky & Pake (1950) and Kubo & Tomita (1954) modified the theory Bloembergen et al (1948) and the modified expression is given below

$$2\pi\nu_c = \alpha\gamma\delta H[\tan\{\pi(\delta H^2-\beta^2)/2.(C^2-B^2)\}]^{-1}$$

where ν_c is the correlation frequency for motion narrowing line, δH is the line width in transition region, B is the line width at temperature higher than transition region, C is the rigid lattice line width, ν is the gyromagnetic ratio and α is a constant equal to $(8 \ln 2)^{-1}$. As usual Arhennius expression is assumed

$$\nu_c = \nu_0 \exp[-E_R/kT],$$

where E_R is the activation energy for motion. Taking $B = 1.504$ gauss, $C = 15.58$ gauss from line width temperature curve (figure 4) the values of ν_c at different temperatures were calculated. A plot of log ν_c against $1/T$ gives a straight line and its slope gives the activation energy E_R which is nearly 26 K.cal/mole.

A linear relationship was observed between 415°K and 445°K, a temperaure range which includes the line width transition. The calculated value of ν_c just below 453°K is $\sim 7.4 \times 10^4$C/S.

6.1. *Second Moment and Molecular Structure*

It has been pointed out that Hvoslef model was not consistent with his observations. The error was detected when a fantastic value of intramolecular contribution to the second moment was obtained using the coordinates of hydroxy hydrogen given by him. In the present work it has been found that there is an agreement between experimental and theoretical values of second moment if we postulate that hydroxy hydrogen is nearer to O_1 than O_2. It has been assumed that hydroxy hydrogen lies exactly in the plane defined by the oxygen atoms. The direction of the OH bond however deviates by 6° from the line connecting the oxygens, thus making the C–O–H angle 110°. This feature is very important in the determination of the position and moment of the hydroxy hydrogen atom. With the second possibility there would be an obvious large deviation from linearity of O—H—O which again supports the first possibility which is also favoured from packing considerations.

The plateau A, B shown in figure 3 represents the measured rigid lattice second moment of the pentaerythritol molecule, where all the effective molecular motion has been frozen. The experimental values of about 28.1 gauss^2 is in good agreement with the calculated second moment of 27.02 ± 1.0 gauss^2. Thus we find that our assumed model is consistent with X-ray, Raman and neutron diffraction studies.

6.2. *Intramolecular Motion of Hydroxyl Group*

It has been pointed out by Andrew (1955) that any reduction in the value of second moment with rise of temperature indicates the presence of some sort of motion in the molecule. Further it has been indicated by Agrawal & Gupta (1967) that if any discontinuity in second moment *vs.* temperature curve is observed before the transition temperature, the possibility of intramolecular motion of the substituent group cannot be ignored. They have observed intramolecular motion of hydroxyl group in a number of organic solids such as alcohols, quinols and naphthols.

Estermann (1929) using a molecular beam experiment, has indicated that the pentaerythritol molecule possesses a dipole moment and since it is a molecule of space group ($I\bar{4}$) which can not have a dipole moment, therefore, this dipole moment can be attributed to the intramolecular motion within the solid. Furthermore Sidgwick (1933), has also obtained a large value of the dipole moment which has been ascribed to the association of hydroxyl groups. Gilbert & Londsdale (1956) have also reported the existence of some sort of intramolecular motion in pentaerythritol molecule.

This anomaly receives further support from infra-red studies by Ellis & Bath (1939), Raman studies by Nayar (1938) and neutron diffraction studies by Hvoslef (1958).

The anomaly may be explained in an alternative way *i.e.*, by assuming change in crystal structure at low temperature. It may be possible that owing to thermal expansion water molecule may enter in the expanded lattice at about 235°K and may start diffusing, causing a reduction in the observed value of the second moment. In our observations the second moment again increases, which corresponds to the state when water molecules settle down in vacancies due to crystal imperfections and the persistence of secondary hump may be explained as due to water molecule sufficiently free to rotate in the vacancy.

The portion *DE* of the curve probably corresponds to rotational oscillation of molecules. This type of motion is exhibited by molecules which occupy closely spaced energy levels.

6.3. *Rotational Transition Effect of Hydrogen Bonding*

6.3.1. *Solid-solid phase transition*

Round about 434°K the second moment has steady value over a narrow range of temperature of a few degrees only. There is an obvious discontinuity of measured second moment and line width at the above temperature giving a clue to the molecular motion. The most likely molecular motion is the reorientation of each molecule about its *c*-axis, which is the symmetry axis in this case.

It has been shown by Gutowsky & Pake (1950), that the effect of such motion on the intramolecular contribution to the second moment is to reduce each term r_{jk}^{-6} in the equation

$$S = 716.15N^{-1} \sum_{j>k} r_{jk}^{-6} \text{ gauss}^2,$$

by a factor

$$\tfrac{1}{4}(3\cos^2 r_{jk} - 1)^2,$$

where r_{jk} is the angle between the intramolecular vector and the reorientation axis. Making use of this factor, it is found that the rotating intramolecular contribution to the second moment is reduced from 14.6 gauss^2 to about 5.7 gauss^2.

There is no simple theory for finding the corresponding reduction of the intermolecular contribution. Andrew & Eades (1953) have developed a theory to meet this requirement but it is very complicated in application. However, it is possible to get an approximate estimate of the inter-molecular contribution by comparing the intra and intermolecular contribution ratios of other similar substances such as cyclohexane (Andrew & Eades 1953). In cyclohexane, the ratio of the reduced intra- and inter-molecular contribution to the second moment is about 1.4. Thus a value of about 7.2 gauss^2 for the reduced intermolecular contribution is not unreasonable. This gives the total reduced second moment of about 12.9 gauss^2 which is in satisfactory agreement with the experimental value of about 12.86 gauss^2, thus clearly supporting the view that the rotation about the symmetry axis is responsible for the narrowing of the spectrum line.

6.3.2. *General molecular rotational transition*

A discontinuity of the measured second moment and line width at temperature about 453°K is observed and second moment value is reduced to nearly 0.5 gauss^2 (plateau *GH*), which appears to be almost entirely intermolecular in origin. The sharp fall in second moment and line width from about 17.5 gauss^2 to about 0.5 gauss^2 and from about 12.22 gauss to 1.5 gauss respectively is accompanied by change in the crystal structure from tetragonal to cubic which was first observed by Ebert (1931) at about 453°K. This means the molecules are now in a position to reorient about other axes besides the symmetry axis. The heat of transition of pentaerythritol is about 10.5K cal/mole (Nitta *et al* 1950). This clearly indicates an increase in molecular freedom; besides an increase in volume of about 9.08% which accompanies the phase transition should bring about a reduction of the barriers which hinder reorientation.

The experimental value of the second moment indicates that the orientation may be of a general character and consequently the molecules must reorient about other axis besides the symmetry axis it should not be concluded that the molecule is in a state of continuous motion about its centre of gravity. The theoretical value of second moment (0.56 gauss^2) is in good agreement with the observed value (0.5 gauss^2) in the temperature range between 453°K and 475°K. Dielectric,

specific heat and conductivity measurements are also consistent with the view that there is considerable molecular reorientation above 453°K.

6.3.3. *Rotational Transition Relation to H-bonding*

The internal motion in the tetragonal form of pentaerythritol seems to be possible only when hydrogen bonds in the molecular layers are broken. It seems logical to postulate that at the high temperature the energy of the molecular transition is caused by hydrogen bonding. Energy of each hydrogen bond has been estimated to be of the order of 5.5K cal/mole (Nitta *et al* 1950) and since there are four intermolecular hydrogen bonds per molecule, our calculated value of the activation energy of about 26K.cal/mole associated with rotation is not insufficient to break all the hydrogen bonds in the crystal. The high value of the activation energy may also be attributed to the constraints present in the crystal. The activation energy estimated by d.c. conductivity measurements (Kiriyama *et al* 1954) is about 20K.cal/mole. Further it is reported (Nitta *et al* 1950) that the observed heat of 10.5K.cal/mole for the transition is not sufficient to break all the hydrogen bonds in the crystal for rotation of the molecule when there are four hydrogen bonds per molecule, the calculated energy of each hydrogen bond being of the order 5.5K.cal/mole. According to them this amount of heat is partly due to the difference of degree of hydrogen bonding in tetragonal and cubic form.

It is interesting that the rotational activation energy is of the same order as the heat of sublimation (Kiriyama *et al* 1954). Usually one expects E to be somewhat less than the heat of sublimation. The equality of E and heat of sublimation may be taken as direct proof of the fact that the binding of the crystal and barrier of rotation is due to the strong hydrogen bonds. Obviously two processes are taking place. The surface molecules are subliming while the internal molecules are rotating, the rates of two phenomena being different. In reorienting inside the crystal a molecule does not rupture the H bond but merely distorts them or tunnels through the barrier they present to the process of reorientation. Steric interactions also contribute their share to the activation energy.

In the line width transition region the molecules reorient at very infrequent intervals compared to the time to make a reorientation. Hence molecules are reorienting independently of one another, meaning thereby that no two neighbouring molecules are in a state for simultaneous reorientation. Thus the molecules would have to overcome or tunnel through the barrier due to all 24 hydrogen bonds attached to it and not only 12 for a molecule to orient in a general manner. However, the molecule would naturally like to reorient about any axis is obviously parallel to C-axis which in this case is the symmetry axis. The fact that the protons on neighbouring molecules are hindered from approaching one another could then explain the low value of second moment at high temperature.

6.4. *Self Diffusion*

The intra molecular contribution to the second moment is reduced to zero in the case of the most general form of reorientation of molecules about fixed centres of mass, leaving an inter molecular contribution of the order of 1 gauss^2. The absence of this contribution may also mean that the centres of mass are not fixed. X-ray and thermal studies lend enough support to our interpretation (large entropy). Above 474°K the second moment shows a further tendency to decrease. Unfortunately due to experimental difficulties at high temperatures, regarding the possibility of rapid decomposition as well as sublimation near the melting point, the observation at higher temperature could not be extended. This further decrement in the second moment clearly indicates a further increment in molecular freedom. This is supported by the relatively small latent heat of fusion, 1.7K cal/mole. Kriyama *et al* (1953) observed in their dielectric study that the dielectric phenomenon is somewhat unusual at higher temperatures than the transition. Their unexpectedly large observed values of dielectric constant and d.c. conductivity may presumably be due to the possibility of molecules diffusing through the crystal lattice. As the melting point is approached vacancies in thd lattice are formed and self diffusion is most likely to occur by the movement of the molecules into neighbouring vacancies in the lattice. The movement of the molecules must at least be of the order of their spacing in the lattice, if the local magnetic field is to be completely averaged out.

As mentioned by Andrew & Eades (1953), Seitz (1951) has described that the frequency of pumping of the molecule into an adjacent vacancy is roughly given by $f\exp(Q/RT)$ where f is the vibrational frequency of molecule in the lattice. If at about 475°K the line width is to be affected by the above process, the jumping frequency should be then of the order of line width. For a vacancy to be created Q may be expected to have a value comparable with the lattice energy. As no experimental values exist for molecular solids our results have to be compared with the experimental values of cubic metals (Andrew 1953). Leclaire (1949) found that Q for self-diffusion is about two-thirds of the lattice energy. The reported value of lattice energy of pentaerythritol is about 30.1 K.cal/mole (Nitta *et al* 1950). A value of the order of 18 K.cal/mole for Q therefore does not look unreasonable, taking jumping frequency of the order 10^4 c/s frequency of vibration of molecule of the order 10^{12}.

6.5. *Impurity Diffusion*

It is generally known that crystalline alcohols occasionally form hydrates and on the other hand sometimes it is very difficult to remove traces of water from crystals. Our observation of the liquid line, on the top of the solid line becoming more sharp at room temperature after heating the sample to about 475°K is attributed to the diffusion of water molecules as an inherent impurity in

the sample. Evidence of this fact is obtained by X-ray investigations (Nitta & Watanabe 1939) which show a slight fall in the thermal expansion coefficient along the C axis, which the author, correlates with the evolution of water intimately combined with the crystal, water molecules being sandwiched here and there between the molecular layers parallel to the C plane. Further support is obtained by the experimental results of Nitta *et al* (1950). They found that when a transparent crystal of pentaerythritol was heated in a closed glass tube at about 403°K, it turned opaque. They also tested the evolution of water from the crystal at about the same temperature on heating the sample under high vacuum using an oil manometer. It is reported that the sample can be purified by fractional sublimation.

Besides, further support to our interpretation is obtained from the fact that our observed transition point at 453°K, for the sample containing water molecule as impurity, is in perfect agreement with the transition point determined by thermal studies using a sample in which water traces have not been removed previously.

Similar diffusion of impurities was obtained for hexamethylene tetra-amine by Smith (1962) who calculated after Waugh (1958) the contribution of diffusing water to the second moment and hence to T_2. He found a negligible contribution to the line width.

Lugt *et al* (1968) have reported a first-order phase transition at about 458°K corresponding to a loosening of hydrogen bonds. They themselves have stated their measurements do not reproduce very well, probably because of the bad heat conductivity of the sample giving rise to large temperature inhomogeneities. As in the present investigations elaborate precautions have been taken to ensure uniform temperature over the sample, it can be reasonably assumed that the results obtained reflect the true state of affairs existing inside the sample under investigation. The observations of Lugt *et al* (1968) also reported only one phase transition thereby indicating that the second transition as observed in the present case owes its origin to the impurity diffusion which has been already explained.

Further it is reported by Nitta & Watanbe (1939) that above 453°K, the crystal structure of pentaerythritol changes from tetragonal to cubic form accompanied by a large volume change at the transition point in which the central carbon atoms are arranged to build a cubic face centred lattice. In this cubic modification the layer structure of the tetragonal form is not retained any more and the mode of hydrogen bonding may not be permanent as in the tetragonal form, but probably forms a three dimensional cage work, in a satistical sense. Owing to thermal expansion, water molecules enter the expanded lattice and may start jumping in a random manner inside the lattice and ultimately settling in some vacancy where it has enough freedom to rotate, thus causing the inherent secondary hump at the room temperature to become sharper after giving heat treatment to the

sample. Further, this mechanism slightly reduces the observed value of the second moment at the room temperature as indicated in figure 2. We cannot consider this as due to a hysterisis effect, as the anisotropic temperatre factor studies (Gilbert & Londsdale 1956) reveal that no such effect has been observed on taking pentaerythritol through a complete cycle of temperature.

The revised fractional coordinates for the hydroxy hydrogen atoms have earlier been reported by these authors (1968). Later Smith (1969) has also reported the results of his investigations on pentaerythritol. The value of the intermolecular contribution to the second moment obtained by him differs by about 5 gauss^2 from the value calculated by the author. The intermolecular contribution was computed after making carefully scaled molecular models and measuring the contacts with utmost accuracy. The measurements have been repeated a number of times and the possibility of any error creeping in the calculations is highly unlikely.

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